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INSULATORS AND CERAMICS

-USSR-

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## FOREWORD

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## INSULATORS AND CERAMICS

-USSR-

[Following is the translation of an article by Candidates of Technical Sciences G.I. Barashenkov and G.N. Maslennikova entitled "Achievements in the Field of High-Voltage Ceramic Materials and Insulator Production Technology" in Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva imeni D.I. Mendeleeva (Journal of the All-Union Chemical Society imeni D.I. Mendeleev), Vol V, No 2, Moscow, May 1960, pages 168-172]

The immense scale of electrification plans mapped out for our country for the next seven-year period has posed a number of important problems before our insulation industry. In the next few years, the production of porcelain, glass, and other types of insulators will have to be tripled. This increase will be attained through the reconstruction of existing insulator plants, and the integration into production of new mechanized factories and workshops.

At the same time, it will be necessary to further improve the quality of insulators. The time has come to master the production of new types of 750-800 kv (kilovolt) insulators, to develop new and improved electro-ceramic materials, and to work out and introduce new high-efficiency technological processes.

The present high-resistance porcelain now being produced is fully adequate for the purposes of manufacturing an extensive and varied selection of electrical porcelain items. First and foremost among these should be porcelain covers of various types used in the arrangement and mounting of insulators and apparatus immersed in oil or other liquid and semi-liquid dielectrics not subject to any significant loads. Next come the 35-kv porcelain line and support insu-

lators capable of withstanding relatively small mainly static or slowly increasing dynamic loads. The strength of the material from which these insulators are made (porcelain) must be increased in order to achieve a reduction in size and weight.

It might also be worthwhile to mention a group of porcelain pieces which are required to withstand significant compression loads. Among these are various types of support insulators, insulating bases, etc. The sufficient strength of the electrical porcelain in its ability to withstand compression, the use of high-precision support-surface polishing methods, and the utilization of elastic packing are all factors which help to make standard-grade porcelain insulators adequate to the requirements of high-voltage applications.

The growing use of long-distance high-voltage transmission lines and new types of 220-500-kv apparatus, however, give rise to the necessity for considerable improvements in the quality of porcelain insulators and other components, the development and introduction of new electroceramics, and the creation of economical and reliable insulator designs.

Transmission voltage and power increases in overhead lines and the problem of reducing the quantities of metal going into line supports have created a need for reducing the size, and at the same time increasing the strength of both suspension and line-coupling insulators.

With the existing mechanical-strength levels of ordinary high-resistance porcelain and the insulator production techniques presently employed, the high electromechanical load suspension insulators now being manufactured are much too large in size and weight; furthermore, the construction of heavy-duty insulators of this type involves certain difficulties.

The erection of  $\pm$  400-kv direct-current electrical transmission lines, as well as the development of electrical railway contact networks has given rise to the necessity for developing durable and reliable ceramic insulators able to withstand wear in a constant high-voltage field.

The manufacture of a number of new types of high-voltage apparatus, e.g. air switches, requires porcelain covers and tubes of great strength and ability to withstand high internal pressures. In a number of cases, ordinary high-resistance porcelain is inadequate to the requirements applicable to this class of components.

Developments in high-voltage mercury rectifier technology and other areas of the electrical industry have created the need for insulators able to function at temperatures of up to several hundred degrees, as well as for insulators which can only be made out of special ceramic materials having specific electrical and mechanical properties at those high temperatures.

### Studies in the Field of High-Voltage Electroceramic Materials

In carrying out studies for the development of new high-voltage electroceramic materials characterized by high mechanical strength, it was borne in mind that the properties of a given material are basically determined by its phase composition. The introduction of new crystalline phases such as  $\alpha$ -alumina, zircon, etc., as well as significant increases in crystalline-phase content in the ceramic material leads to a considerable augmentation of its mechanical strength.

The table lists the names and properties of the newly-developed electroceramic materials to be used in the production of high-voltage insulators and electroceramic components for high-voltage apparatus; data on standard high-resistance porcelain are given in the same table for the sake of comparison.

### Corundomullite Porcelain (1.2) KM-1

This new type of high-resistance porcelain is characterized by high mechanical strength. Its distinguishing property consists in a high crystalline-phase content in the form of corundum and mullite (aluminum silicate refractory). In order to assure fusion of the constituents, divalent metal oxides forming a mobile, easily fusible glass phase are added to the mixture.

The following are the primary raw materials used in the KM-1 mixture: fired industrial-grade alumina, Chasov'yarskaya clay, Prosyonovskiy kaolin, as well as barium, strontium, and calcium carbonates. This mixture has good plastic qualities and lends itself to the usual forming techniques used in the insulator industry.

Corundomullite porcelain is used for high mechanical strength covers and tubes for high-voltage air switches, high-voltage support and line insulators able to withstand large

А Показатели свойств	Б Единица измерения	В Корундо-муллитовый фарфор (KM-1)	Г Глиноземистый фарфор (MG-12)	Д Муллитовый фарфор (K-21)	Е Ашаритовый фарфор (B-44)	Ж Цирконий-фторид (ZrF-35)	З Сподоменитовый фарфор (S-100)	И Нормы по лабораторным фарфорам (M-23)
А Предел прочности при статическом изгибе на образцах диаметром 20 мм	кг/см <sup>2</sup>	1150—1350	900—950	1150	1400—1500	1350—1400	850	550—650
Б на образцах диаметром 10 мм	кг/см <sup>2</sup>	1600—2000	1200—1250	1420—1450	550—650	450—600	—	700—900
В разрыве	кг/см <sup>2</sup>	500—550	400—450	570	2,4—2,7	1,8—3,0	—	280—380
Г динамическом изгибе	кг/см <sup>2</sup>	2,2—2,8	1,9—2,0	—	—	—	—	1,7
Д температурный коэффициент линейного расширения	α · 10 <sup>-6</sup>	3,2—3,8	3,9	—	2,8	3,4	1,7	3,2—4,4
Е 20° ± 200°	°C	—	4,6	—	3,9	3,7	2,1	4,8—6,2
Ж 20° ± 400°	°C	190—210	190	160	200	200—220	550	160
З Термостойкость	°C	15—18	330	140	18—40	250—330	400—450	300—400
И тангенса угла диэлектрических потерь при 50 гц	10 <sup>-4</sup>	7,0	7,0	6,3	6,3	6,2	—	6,5
К диэлектрическая проницаемость	—	—	—	—	—	—	—	—
Л удельное объемное электрическое сопротивление при 20° C	ом · см	10 <sup>12</sup> —10 <sup>14</sup>	2 · 10 <sup>12</sup>	1,5 · 10 <sup>13</sup>	10 <sup>14</sup>	10 <sup>13</sup>	10 <sup>12</sup>	10 <sup>12</sup>
М при 100° C	ом · см	10 <sup>12</sup> —10 <sup>14</sup>	—	—	10 <sup>14</sup>	—	—	—
Н электрическая прочность при 20° C	кг/мм <sup>2</sup>	30—35	29—31	43,0	27—31	30—35	28—30	25—30
О температура обжига	°C	1330—1370	1320—1350	1350—1410	1310—1330	1320—1380	1300—1320	1280—1350
П кристаллическая фаза	—	Корунд, муллит	Корунд, муллит	Муллит	Муллит, корунд	Циркон, муллит	Сподомен, муллит	Кварц, муллит

A = Properties.

B = Units of measurement.

C = Corundomullite porcelain (KM-1).

D = Alumina porcelain (MG-12).

E = Mullite porcelain (K-12).

F = Asharite porcelain (B-44).

G = Zircon porcelain (TS-35).

H = Spodumene porcelain (S-100).

I = Standard feldspar porcelain (M-23).

[Cont'd on following page.]

J = Limits of strength for:  
 K = static bending of samples 10 and 20 millimeters in diameter.  
 L = tensile rupture.  
 M = dynamic bending.  
 N = Temperature coefficient of linear expansion.  
 O = Thermal stability.  
 P = Tangent of dielectric loss angle at 50 cps (cycles per second) and 20°C.  
 Q = Dielectric permeability.  
 R = Net specific electrical resistance  
     at 20°C  
     at 100°C  
 S = Dielectric strength.  
 T = Firing temperature.  
 U = Crystalline phase  
 V = Corundum, mullite.  
 W = Corundum, mullite.  
 X = Mullite.  
 Y = Mullite, corundum.  
 Z = Zircon, mullite.  
 A' = Spodumene, mullite.  
 D' = Quartz, mullite.  
 C' = kilograms/centimeter<sup>2</sup>  
 D' = kilocycle per second  
 E' = ohm-centimeters  
 F' = kilovolts/millimeter

mechanical stresses, and also for the production of radio antenna insulators.

### Alumina Porcelain (3) MG-12

This type of porcelain is used in making a wide variety of strong high-voltage insulators, including covers and air ducts for air switches, suspension line insulators able to withstand great mechanical loads, etc. Its crystalline phase consists of corundum and mullite. The primary raw materials making up the MG-12 mixture are industrial-grade fired alumina, Chasov'yarskaya clay, Prosyonovskiy kaolin, and pegmatite.

One favorable characteristic of this composition is the similarity of its working properties to those of the ordinary electrical porcelain mixture. Its ample plasticity permits manufacture of insulators by the usual forming methods. The use of the MG-12 mixture in the making of suspension line insulators has yielded a twofold increase in their strength.

The application of MG-12 alumina porcelain was made possible by studies carried out on the effects of quartz, clayey ingredients, and added quantities of alumina on the properties of high-resistance porcelain. The tests were conducted on a mixture containing 45.3% clayey ingredients, 19.8% quartz, and 33.5% feldspar.

Three groups of test mixtures compounded on the basis of this mixture were investigated.

In the first group, clayey ingredients were kept constant, while the quartz content was varied from 19.8% to 34.7% with a corresponding reduction in the quantity of quartz [sic].

It was noted that an increase in the quartz content of porcelain mixtures yields a certain increase in the mechanical strength of the porcelain ( $\delta_{\text{bending}} = 1150 \text{ kg/cm}^2$  in a composition containing 30.6% quartz, and  $1000 \text{ kg/cm}^2$  in the initial mixture).

The works of some foreign authors (4,5) dealing with investigations on the effects of quartz take note of its favorable role in increasing the mechanical strength of porcelain; this fact is explained by structural stresses in the material which arise during the cooling process following firing, and which bring about an increase in its mechanical strength. A more significant increase in the mechanical



strength of porcelain materials was found to result after increasing the clayey ingredients content or adding alumina to the mixture.

In studying the effects of alumina additions in amounts ranging from 3 to 12%, the maximum increase in the static bending strength up to 1200-1300 kg/cm<sup>2</sup> in the MG-12 mixture was obtained with the 12%-alumina mixture. This particular composition also exhibited the greatest value for the elasticity modulus, which was equal to  $1.030 \times 10^6$  kg/cm<sup>2</sup>; the corresponding figure for the initial mixture was  $0.840 \times 10^6$  kg/cm<sup>2</sup>.

The dielectric strength of all test mixtures was found to lie in the range of 40-45 kv/mm. Its high values are explained by the high dispersion of individual ingredients.

The positive results in the areas indicated have been confirmed by the studies of foreign authors (6-8).

#### Mullite Porcelain (9) K-21

Further studies in the field of porcelain materials with an increased clayey ingredient content were performed on the basis of fired kaolin. Materials of this type are characterized by a more homogeneous microstructure, and a high crystalline-phase content (up to 80%) consisting of mullite crystals exclusively.

In order to obtain the desired technological properties from the mixture with reference to technological processes used in the insulator industry, the greater part of the kaolin is added to the mixture in the fired state.

The favorable results obtainable in the application of electrical porcelain mixtures with an increased clayey ingredient content are also noted in the works of foreign authors (7).

#### Asharite Porcelain (10)

This type of porcelain gets its name from the asharite ore introduced into its primary mixture. It is intended for use in producing high-resistance insulators with great mechanical strength. Since furthermore it exhibits a low value for the tangent of  $\delta$  at high frequencies due to its low alkaline salt content, it can also be employed for making high-frequency insulators.

In comparison with feldspar electrical porcelain, anharite porcelain is characterized by a low value for  $\tan \delta$  at a frequency of 50 cps, while a sharp increase in  $\tan \delta$  in proportion to temperature begins to appear at considerably higher temperatures.

#### Zircon Porcelain (11)

This type of electrical porcelain was obtained as a result of studies on the effect of replacing quartz with zircon in feldspar porcelain. Its crystalline phase consists of zircon and mullite.

This replacement was suggested by the differences in the behavior of mullite and quartz which enter into the structure of ordinary porcelain upon heating; one such difference is exhibited in their widely divergent coefficients of thermal expansion, which is small in the case of zircon and mullite.

Among the specific properties of this type of porcelain are great mechanical strength, increased thermal stability in comparison to that of ordinary electrical porcelain, as well as good dielectric strength.

The zircon porcelain mixture is characterized by a broad fused-state interval, satisfactory forming and drying qualities, and may be used in making insulators by the usual methods.

#### Spodumene Porcelain (12)

Studies carried out on the effects of adding lithium-containing minerals spodumene and lepidolite to electrical porcelain made it possible to obtain a new ceramic material -- spodumene porcelain.

The introduction of spodumene, which has a negative coefficient of thermal expansion, into porcelain in place of feldspar materials yielded a porcelain with high thermal stability (500-550°), a low coefficient of thermal expansion ( $1.7 \times 10^{-6}$  in the 20-100° range), and sufficient mechanical strength. The crystalline phase of this porcelain consists of  $\beta$ -spodumene and mullite.

A relation of direct proportionality was found to hold between the thermal stability of porcelain and its lithium oxide content.

The firing temperature for spodumene porcelain (S-100)

is 1320°, while its fused-state interval is 40°.

In contrast to standard feldspar porcelain, spodumene porcelain must be fired in a slow-reduction gas atmosphere at a quicker cooling rate, equal to 300° per hour in the temperature interval 1320-1000°.

Lesser cooling rates in the indicated interval result in an excessive crystallization of the glass phase and considerable crystal growth; this gives the porcelain high thermal stability but turns out to be unsatisfactory because of the low values for the penetrative gradient.

On the other hand, excessively rapid cooling does not allow the crystallization processes to proceed to a sufficient degree.

The spodumene porcelain mixture is analogous in its processing qualities and behavior to standard feldspar porcelain.

#### Studies in the Field of Standard Electrical Porcelain and Insulator Manufacturing Technology

In the search for new ways of improving the properties of feldspar insulator porcelain, there have been studies made recently on the effects of quartz and feldspar dispersion on mixture properties (13).

The earlier investigations performed on industrial porcelain (14,15) served to indicate the favorable effect of increasing the dispersion of the primary raw materials on the mechanical strength of the porcelain.

Recent work done on electrical porcelain mixtures (5) has also demonstrated the advisability of effecting thorough dispersion of ingredients.

Studies of the group of electrical porcelain mixtures with mean surface diameter of the feldspar and quartz ranging between 1.5 and 19.4 $\mu$  (microns) have shown that the increased dispersion of the indicated fusion materials significantly increases both the mechanical and dielectric strength of the porcelain. Samples made of highly-diffused mixtures exhibited a temporary bending strength of up to 1300 kg/cm<sup>2</sup>, while the dielectric strength reached 46 kv/mm.

Increased quartz and feldspar dispersion results in a significant lowering of mixture fusion temperatures. The difference in the temperatures corresponding to the upper and lower dispersion limits of the samples tested reached 100°.

An increased dispersion also broadens the fused-state interval of the mixtures. Mixtures of greater dispersion are characterized by a greater temperature interval over which specific weight and shrinkage remain maximum.

An increased dispersion lowers the actual porosity of the porcelain, increases its glass content, and is effective in giving it greater structural homogeneity.

At the same time, greater dispersion of the fusing ingredients leads to certain undesirable changes in the properties of an electrical porcelain mixture.

Thus, the use of hyperfine fusing materials (leaving no residue on an 006 sieve -- with a mean surface diameter of the particles equal to  $5\mu$ ) reduces the filtering capability of the mixture, increases its actual water-holding capacity, critical moisture content, and moisture gradient, and gives the half-finished product greater porosity, thus reducing its mechanical strength.

All of these changes in the properties complicate the drying process for the half-finished product and hinder the actual application of the indicated advantages of hyperpulverized fusing materials under the present conditions of insulator production. In conformance to these conditions, the optimum degree of fineness was shown to be such that sifting through an 006 sieve would leave a 0.5-1.0% residue. This particular level of granulation results in a considerable increase in both the mechanical and dielectric strength of the porcelain, and at the same time does not lead to significant changes in the technological properties of the mixture.

Some insulator factories make use of a sufficiently rough fusing material granulation, one which leaves 8-9% on an 006 sieve, in their porcelain mixtures.

One of the reasons which complicate the finer granulation of porcelain ingredients at the factories is the low efficiency of the ball-mill grinding balls. This is the reason that studies on the intensification of the milling process are assuming such importance. Among the most recent studies in this area it is necessary to mention those concerned with developing new mixtures and technological production methods for artificial ceramic ball-mill balls and the use of alumina mill balls in grinding porcelain mixtures (16,17). Two ceramic materials with a high alumina content, M-13 and M-21, which have already been developed are characterized by an increased specific weight and resistance to wear.

The M-13 material contains 40% alumina, has a specific

weight of 2.9 grams/centimeter<sup>3</sup>, and a firing temperature of 1380°.

Material M-21 contains 70% alumina, has a specific weight of 3.2 grams/centimeter<sup>3</sup>, and requires a somewhat higher firing temperature (1440°).

The comparative testing of milling balls made of flinty crush rock, white stone castings, as well as of the alumina-ceramic material developed earlier (18,19) called "uralite" (specific weight -- 3.0), and the M-13 and M-21 materials for grinding porcelain mixtures showed that the use of alumina-ceramic balls increases considerably the efficiency of ball mills, with a concomitant reduction in grinding-surface wear.

The greatest efficiency was attained with balls made out of the M-21 material which had the greatest specific weight of the materials tested.

The use of the industrially-produced uralite grinding balls reduces the grinding time from 10-11 hours (with flinty crush rock heads) down to 4-5 hours. The resultant wear of the uralite mill balls turned out to be twice as small as that of the flinty crush rock balls. The introduction into industry of uralite-head mixture grinding has created the possibility of significantly improving the quality of electrical porcelain mixtures through increased dispersion without the necessity of installing additional mill-grinding apparatus.

A roughly-ground mixture, in addition to lowering the dielectric strength of the porcelain, requires the maintenance of an increased feldspar content in order to fuse properly at a given temperature. This, in turn, results in a very high glass-phase content in the porcelain structure, thus lowering its ability to withstand impact bending and reducing its stability in the presence of sharp temperature fluctuations.

Reducing the feldspar content in the porcelain mixture, on the other hand, gives rise to the necessity for higher firing temperatures which is undesirable for the insulator factories.

A lowering of the fusion temperature for electrical porcelain mixtures obtained through the use of greater fusing material dispersion and finer grinding has created actual prospects for obtaining a further improvement of electrical porcelain properties by means of compositional adjustment.

The basic direction of such adjustments apparently lies in reducing the glass-phase content in porcelain by

lowering the feldspar content, and through slight increases or even the retention of firing temperatures presently in use at the insulator factories.

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